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FULL PAPER

Hydrazo-keto and azo-enol tautomerism in organometallic palladacycles. New bidentate monoanionic and tridentate bianionic ligands

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The action of $PdCl_2$ on phenylhydrazones derived from 2-oxopropionaldehyde, benzoylformaldehyde or butane-2,3-dione led to dinuclear metallacycles **1** [{Pd[2-(NR^{4}N=CR^{3}CR^{2}O)-5-R^{1}C$_6$H$_3$]Cl}$_2$] (R^1 = H, Br, NO_2 or MeO; R^2 = Me or Ph; R^3, R^4 = H or Me). Compounds **1** reacted with PPh_3 to afford [PdCl{κ*C*,κ*N*-(C–N)}(PPh_3)] **2** or [PdCl{κ*C*-(C–N)}(PPh_3)$_2$] **3** (C–N being the metallated hydrazone) which contain one or two phosphine molecules per metal atom respectively, depending on the steric hindrance of the N-donor ligands. The structure of [Pd{2-(NHN=CHCOMe)-5-$O_2NC_6H_3$}Cl(PPh_3)] has been determined by X-ray diffraction. The bond distances and angles are similar to those reported for related metallacycles. The distance N(1)···O(1) [2.631(4) Å] indicates the presence of a strong intramolecular hydrogen bond between the NH and COMe groups. The C(8)–O(1) [1.222(5) Å], C(8)–C(7) [1.470(5) Å], C(7)–N(2) [1.304(4) Å] and N(1)–N(2) [1.342(4) Å] bond lengths indicate that the complex **3** exists mainly in the keto-hydrazo form. The action of NaOMe on the PPh_3 or (PPh_3)$_2$ complexes in MeOH afforded deep violet compounds which do not contain chlorine atoms. The analytical data, IR and NMR spectra showed that deprotonation of the NH group had taken place to give [Pd{2-(N=NCR^3=CR^{2}O)-5-R^{1}C$_6$H$_3$}(PPh_3)], by means of an hydrazo-keto azo-enol tautomerization.

The equilibrium between the hydrazoketo and azoenol forms of organic molecules, containing the HN–N=C–C=O group, is well known and because of their importance in the dyestuff industry and as acid–base indicators this process has been studied in detail. Furthermore, a very strong intramolecular hydrogen bond has been observed between the N–H and CO fragments in some organic compounds containing this group.[1,2] Strong hydrogen bonds occur due to the fact that the neutral donor and acceptor atoms are connected by a system of π-conjugated double bonds; this system has been referred to as RAHB (resonance-assisted hydrogen bonding). It has been used successfully to explain intra- and inter-molecular O–H···O hydrogen bonds in compounds containing the β-diketo enol fragment[3] and to explain N–H···O bonds in molecules containing the HN–N=C–C=O fragment.[4]

Palladium complexes with polydentate ligands have been extensively studied,[5,6] and it has recently been shown that palladacycles with anionic bidentate P–C or N–C ligands are efficient catalysts for a wide range of processes.[7] Following our studies on organometallic complexes derived from hydrazones[8] we report here the synthesis of new palladacycles containing phenylhydrazones derived from 2-oxopropionaldehyde, benzoylformaldehyde or butane-2,3-dione. In these palladacycles the organic fragment acts as a bidentate monoanionic ligand in the hydrazoketo form, and a strong intramolecular hydrogen bond between the N–H and the C=O fragments was observed in some cases, depending on the nature of the substituents in the organic ligand. These results show that RAHB model can also be used to explain hydrogen bonds in organometallic compounds. Moreover, deprotonation of the N–H bond of these complexes afforded new palladacycles, in which the organic fragment acts as a terdentate bianionic ligand, in the azo-enol form, by means of a tautomerization process unusual in organometallic derivatives.

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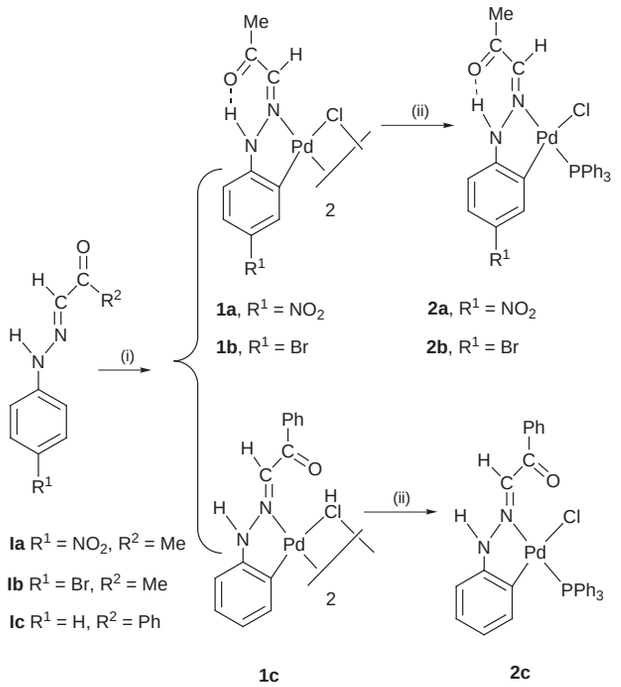
Results and Discussion

The action of $PdCl_2$ on phenylhydrazones derived from 2-oxopropionaldehyde, benzoylformaldehyde or butane-2,3-dione leads to the cyclopalladated complexes **1** (see Schemes 1 and 2). The new compounds were characterized by elemental analysis, IR and ^{1}H NMR spectra. Owing to their insolubility, the NMR spectra were recorded in the presence of C_5D_5N, which affords the mononuclear complexes [PdCl{κ*C*,κ*N*-(C–N)}(C_5D_5N)]. (The spectra of **1h** were not recorded because it is insoluble, even in the presence of pyridine.) The aromatic protons of the metallated phenyl group are shifted to high field in the spectra of all the new compounds obtained, showing a *cis* arrangement between this ring and the pyridine ligand.[6g] The signal assigned to the NH proton appears strongly shifted to low fields (δ 13.9–14.5), in the spectra of the mononuclear complexes [PdCl{κ*C*,κ*N*-(C–N)}(C_5D_5N)], C–N being the metallated hydrazones **Ia** and **Ib**, indicating a strong hydrogen bond between the MeCO and the NH groups.[4,8a] Moreover the signal assigned to the methine proton in these compounds is shifted to low field in relation to that of free C–N. This shift can be explained by the paramagnetic anisotropy of the palladium atom and indicates that the metallated phenyl ring and the COMe group adopt a *cis* disposition around the C=N bond, thus an *E–Z* isomerization occurs during the cyclometallation

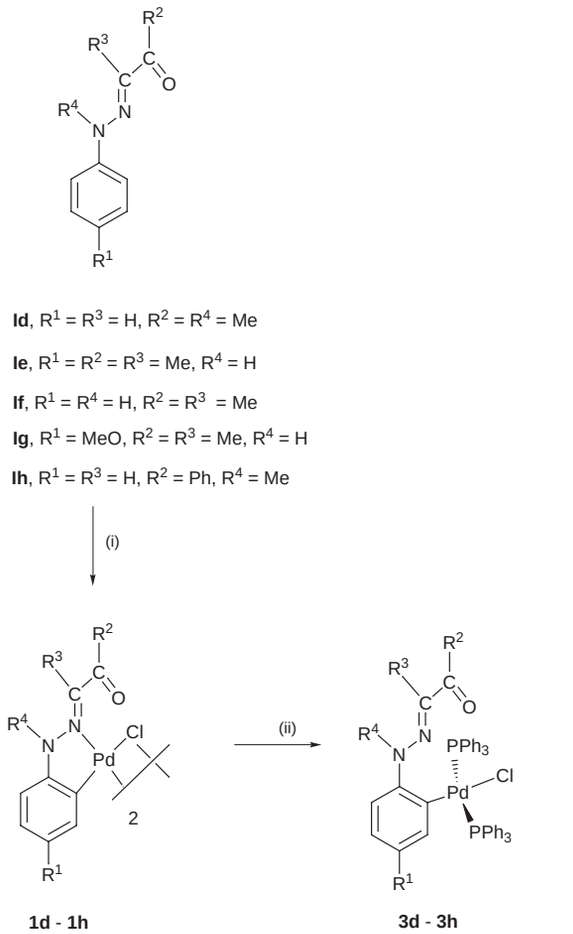


Scheme 1 (i) $PdCl_2$, EtOH, room temperature, 3 d; (ii) PPh_3 (2 equivalents), $CHCl_3$, 30 min

of **Ia** and **Ib**,‡ as has been reported for similar cyclopalladated derivatives from imines.[9] In contrast, the signal assigned to the NH proton appears at δ *ca*. 9.3–9.0 and the HC=N proton appears at δ *ca*. 7.3–7.0, in the spectra of [PdCl{κ*C*,κ*N*-(C–N)}(C_5D_5N)], C–N being the metallated hydrazones **Ic** and **Ie–Ig**. These data show that in these compounds there is no interaction between the MeCO and the NH groups and that the ligand adopts the *E* configuration.

The dinuclear compounds **1** react with PPh_3 affording the cyclometallated complexes [PdCl{κ*C*,κ*N*-(C–N)}(PPh_3)] **2a–2c** or compounds [PdCl{κ*C*-(C–N)}(PPh_3)$_2$] **3d–3h**, containing two phosphine molecules per metal atom, depending on the steric hindrance of the N-donor ligands (see Schemes 1 and 2). The new compounds obtained were characterized by elemental analysis, IR and ^{1}H and ^{31}P NMR spectra. In several cases COSY and FAB mass spectra were recorded to complete the characterization. Aromatic protons of the palladated ring in **2** appear shifted to high field in the ^{1}H NMR spectra indicating a *cis* arrangement of the phosphine and the metallated carbon atom.[6g] The ^{31}P-{^{1}H} NMR spectra of **2a–2c** display a singlet at δ 42.0 to 44.0 showing a *trans* arrangement between the phosphine and the imine nitrogen.[6g] Steric factors have been invoked to explain the difficulty in the synthesis of related metallacycles containing one molecule of PPh_3 per metal atom.[10] In particular, it is known that the presence of a substituent adjacent to the M–C bond prevents the formation of the PPh_3-containing metallacycles and only metallated compounds [MX{κ*C*-(C–N)}(PPh_3)$_2$], without a metal–nitrogen bond, can be obtained. Steric factors can also explain that in this study the cyclopalladated derivatives [PdCl{κ*C*,κ*N*-(C–N)}(PPh_3)] were only obtained if $R^3 = R^4 = H$. Owing to the planarity of the metallacycle, the C–NR^4–N=CR^3–C fragment is also planar (see crystal structure of **2a**) and, in the *E* isomers, the R^3 and R^4 groups are in close proximity, as can be observed by using molecular models. In consequence, metallacycles **2** can only be obtained if $R^3 = R^4 = H$.

‡ It should be noted that a mixture of the *E* and *Z* (with an intramolecular N–H···O=C bond) isomers is observed in free hydrazones **a** and **b** by proton NMR spectroscopy in $CDCl_3$ solutions. In contrast, all the other free hydrazones exist in solution in the *E* form, without the intramolecular hydrogen bond.



Scheme 2 (i) $PdCl_2$, EtOH, room temperature, 3 d; (ii) PPh_3 (4 equivalents), $CHCl_3$, 30 min

The signal assigned to the NH proton, in the ^{1}H NMR spectra, appears strongly shifted to low fields (δ 13.9–14.5) for complexes **2a** and **2b**, showing an intramolecular hydrogen bond between the MeCO and the NH groups, as has been confirmed by the crystal structure of **2a** (see below). The RAHB model has been used to interpret the intramolecular hydrogen bond in O=C–C=N–NH fragments.[4] This model proposes that the hydrogen bond and π delocalization are linked by a synergistic mechanism in which the resonance between O=C–C=N–NH and $^-$O–C=C–N=N$^+$H forms produces fractional charges on the terminal O and N atoms that have the correct sign for strengthening the intramolecular hydrogen bond. It can explain the fact that the intramolecular bond is not formed in **e**, **f**, or **g** derivatives, which present a MeC=N fragment, because the presence of a donor group on the methine carbon prevents the electron flux from the aminic nitrogen to the oxygen atoms. Moreover, when R^2 = Ph (compounds **c**) this phenyl may compete with the C=O group for the π electron density, which can explain why the intramolecular hydrogen bond is not observed in **1c** or **2c**.

The crystal structure of complex **2a** has been determined (Fig. 1). Bond lengths and angles are listed in Table 1. The structure consists of discrete molecules separated by van der Waals distances. The bond distances and angles are similar to those reported for related metallacycles.[8] The palladium atom is in a slightly distorted square-planar environment co-ordinated to phosphorus, carbon, chloride and the imine nitrogen atom. The co-ordination plane shows some tetrahedral distortion, the deviations from the mean plane being −0.112, +0.115, −0.136 and +0.149 Å for P, Cl, N(2) and C(1), respectively. The imine nitrogen and the phosphine molecule adopt a *trans* arrangement. The distance N(1)···O(1) [2.631(4) Å] confirms the intramolecular hydrogen bond between the NH and COMe

Table 1 Selected bond lengths (Å) and angles (°) for complex **2a**

Pd–C(1)	2.010(3)	N(1)–N(2)	1.342(4)
Pd–N(2)	2.103(3)	N(1)–C(6)	1.380(4)
Pd–P	2.2475(8)	N(2)–C(7)	1.304(4)
Pd–Cl	2.3659(9)	C(7)–C(8)	1.470(5)
O(1)–C(8)	1.222(5)	C(8)–C(9)	1.479(6)
C(1)–Pd–N(2)	80.54(12)	C(7)–N(2)–N(1)	121.2(3)
C(1)–Pd–P	94.68(9)	N(2)–C(7)–C(8)	125.0(3)
Cl–Pd–N(2)	93.58(8)	O(1)–C(8)–C(7)	121.3(3)
P–Pd–Cl	92.00(3)	O(1)–C(8)–C(9)	122.8(4)
N(2)–N(1)–C(6)	117.3(3)	C(7)–C(8)–C(9)	115.8(4)

Table 2 Crystal data and structure refinement for complex **2a**

Empirical formula	$C_{27}H_{23}ClN_3O_3PPd$
M	610.30
T/K	293(2)
λ(Mo–Kα)/Å	0.710 69
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	9.475(3)
b/Å	10.4872(10)
c/Å	13.301(2)
α/°	77.012(7)
β/°	83.56(2)
γ/°	87.239(13)
U/Å^3	1279.4(4)
Z	2
D_c/g cm^{-3}	1.584
μ/mm^{-1}	0.927
F(000)	616
Index ranges	$-13 \leqslant h \leqslant 13$, $-14 \leqslant k \leqslant 14$, $-4 \leqslant l \leqslant 18$
Reflections collected	7545
Independent reflections	7444 (R_{int} = 0.1389)
Data, restraints, parameters	7394, 0, 418
Goodness of fit on F^2	1.034
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0467, 0.1260
(all data)	0.0652, 0.1538
Largest difference peak and hole/e Å^{-3}	1.447 and −1.253

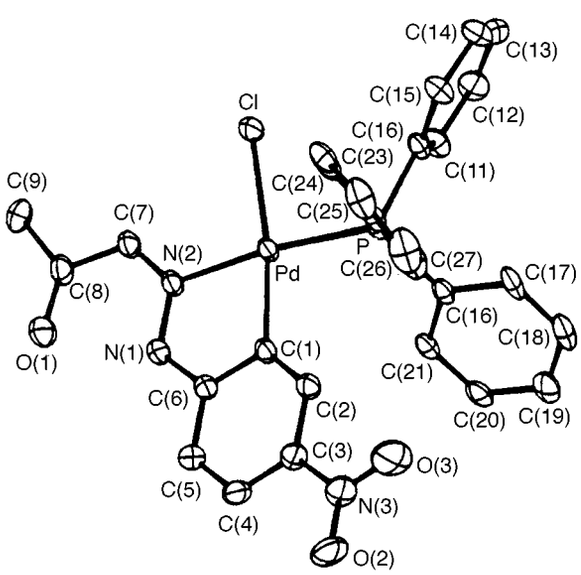
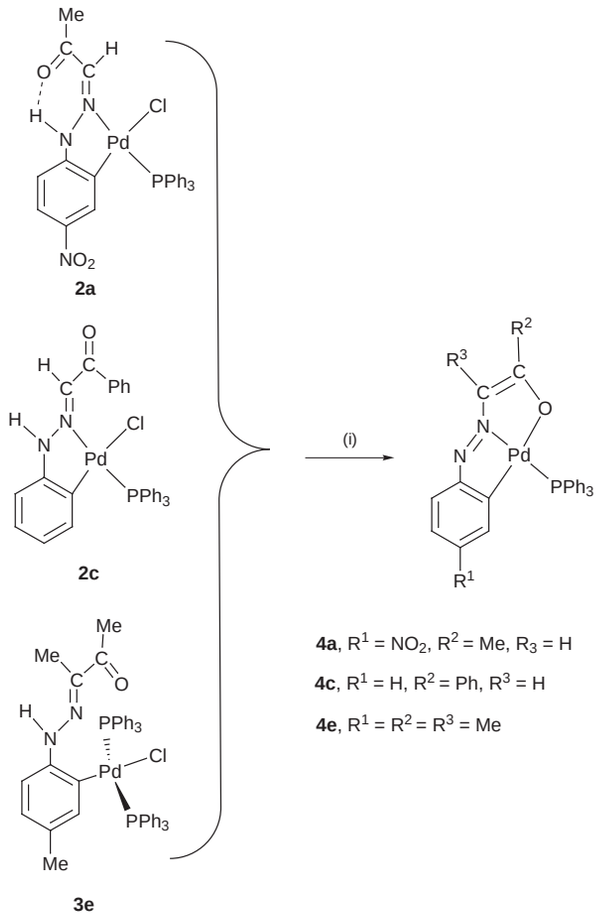


Fig. 1 Molecular structure of complex **2a**

groups. It should be noted that in the closely related metallacycle [Pd{2-[NHN=CHC(O)Me]-3-MeC$_6$H$_3$}Cl(PPh$_3$)] the N···O distance is shorter [2.583(7) Å].[8a] The weakening of the intramolecular hydrogen bond produced by electron-withdrawing substituents in the aromatic ring of analogous free hydrazones has also been explained by the RAHB model.[4b] The



Scheme 3 (i) NaOMe, MeOH, room temperature, 2 h

C(8)–O(1) [1.222(5) Å], C(8)–C(7) [1.470(5) Å], C(7)–N(2) [1.304(4) Å] and N(1)–N(2) [1.342(4) Å] bond lengths indicate that **2a** mainly adopts the keto-hydrazo form.[2,4,8a]

The angles between adjacent atoms in the co-ordination sphere lie in the range 94.68(9) [P–Pd–C(1)] to 80.54(12)° [N(2)–Pd–C(1)]. The smallest of these angles is that between the co-ordinating nitrogen and carbon atoms of the chelated ligand. The metallacycle presents an *exo* structure, because the C=N bond is not contained in the metallacycle, and the hydrazone moiety adopts the Z form, according to NMR data. The N–N=C–C moiety is nearly planar; the torsion angle is 1.2(6)°. The dihedral angles between the hydrazone moiety and both the metallacycle and the co-ordination plane are smaller in **2a** (1.76 and 6.41° respectively) than in related hydrazone metallacycles.[8b] It seems that the intramolecular hydrogen bond between the H–N and C=O fragments reinforces the planarity of the hydrazone cyclometallated derivatives.

The action of NaOMe on complexes **2a**, **2c** and **3e** in MeOH affords deep violet compounds which do not contain chlorine atoms and, when the reaction was performed with **3e**, the formation of free triphenylphosphine was also observed. The analytical data, the infrared spectra (absence of the strong bands of C=O and C=N bonds and a weak band at *ca.* 1420–1470 cm^{-1}, assigned to the N=N group) and the NMR studies show that deprotonation of the N–H bond takes place to give **4** (Scheme 3), by means of a hydrazo-keto azo-enol tautomerization. We have previously reported[8a] this reaction with palladacycles containing 2-oxopropionaldehyde phenylhydrazones [Pd{2-[NHN=CHC(O)Me]-3-RC$_6$H$_3$]Cl(PPh$_3$)] and here we show that this reaction is quite general because it can also take place with substituted hydrazones and even with the compound **3e** [PdCl{κ*C*-(C–N)}(PPh$_3$)$_2$], without the Pd–N bond.

In conclusion, the results described in this work show the importance of the substituents of the hydrazone moiety in the

reactivity of the metallacycles, as well as in the ability of the HN–N=C–C=O fragment to form hydrogen bonds. These results also show that the RAHB model can be used to explain hydrogen bonds in organometallic compounds.

Experimental

Proton NMR spectra at 200 and 500 MHz and $^{31}P-\{^{1}H\}$ at 101.26 MHz were recorded, respectively, on Varian Gemini 200, VXR 500 and Bruker DRX 250 spectrometers. Chemical shifts (in ppm) were measured relative to $SiMe_4$ for ^1H and to 85% H_3PO_4 for ^{31}P. The solvents used were $CDCl_3$ in ^1H and $CHCl_3$ in ^{31}P. Microanalyses were performed at the Institut de Química Bio-Orgànica de Barcelona and the Serveis Científico-Tècnics de la Universitat de Barcelona.

Solvents were dried and distilled before use and hydrazones were obtained according to procedures described elsewhere.[11]

Crystallography

Data collection. An equidimensional crystal (0.2 × 0.2 × 0.2 mm) of complex **2a** was selected and mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Unit-cell parameters were determined from automatic centering of 25 reflections ($12 \leqslant \theta \leqslant 21°$) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo-Kα radiation, using the ω–2θ scan technique. 7444 Reflections were measured in the range $1.58 \leqslant \theta \leqslant 29.96°$, 6190 were assumed as observed applying the condition $I \geqslant 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Corrections were made for Lorentz-polarization but not for absorption.

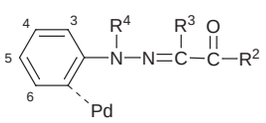
Structure solution and refinement. The structure was solved by Patterson synthesis, using the SHELXS computer program[12] and refined by full-matrix least squares, with SHELXL 93,[13] using 7394 reflections (very negative intensities were not assumed). The function minimized was $\Sigma w[|F_o|^2 - |F_c|^2]^2$, where $w = [\sigma^2(I) + (0.0965P)^2 + 0.3375P]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f' and f'' were taken from ref. 14. The extinction coefficient was 0.0008(10). All hydrogen atoms were located from a difference synthesis and refined isotropically. The final R (on F) factor was 0.046, wR (on $|F|^2$) = 0.126. Maximum shift/e.s.d. = 0.1, mean shift/e.s.d. = 0.0.

CCDC reference number 186/945.

See http://www.rsc.org/suppdata/dt/1998/1781/ for crystallographic files in .cif format.

Preparations

Compounds 1. A stirred suspension of $PdCl_2$ (1.69 mmol, 0.3 g) in ethanol (30 cm^3) was treated with the corresponding hydrazone (1.69 mmol) for 3 d at room temperature. The solid obtained was filtered off, washed with ethanol (2 × 15 cm^3) and dried *in vacuo* to afford an orange or brown solid.



Complex **1a**. Yield 291 mg (50%) (Found (Calc. for $C_9H_8ClN_3O_3Pd$): C, 30.3 (31.13); H, 2.3 (2.32); N, 12.1 (12.11)%]. ^1H NMR: **1a** + C_5D_5N, δ 13.89 (s, 1 H, NH), 8.20 (s, 1 H, HC=N), 7.88 (dd, J_{HH} = 8.75, 2.0, 1 H, H^4), 6.89 (d, J_{HH} = 2.0, 1 H, H^6), 6.71 (d, J_{HH} = 8.5 Hz, 1 H, H^3) and 2.36 (s, 3 H, CH_3CO).

Complex **1b**. Yield 492 mg (76%) [Found (Calc. for $C_9H_8BrClN_2OPd$): C, 28.7 (28.43); H, 2.2 (2.12); N, 7.2 (7.37)%]. ^1H NMR: **1b**+C_5D_5N, δ 13.94 (s, 1 H, NH), 8.02 (s, 1 H, HC=N), 7.06 (dd, J_{HH} = 8.2, 1.8, 1 H, H^4), 6.50 (d, J_{HH} = 8.0, 1 H, H^3), 6.07 (d, J_{HH} = 1.8 Hz, 1 H, H^6) and 2.26 (s, 3 H, CH_3CO).

Complex **1c**. Yield 560 mg (91%) [Found (Calc. for $C_{14}H_{11}ClN_2OPd$): C, 46.1 (46.15); H, 3.1 (3.04); N, 7.6 (7.69)%]. ^1H NMR: **1c**+C_5D_5N; δ 9.00 (s, 1 H, NH), 8.07 (d, J_{HH} = 8.6, 2 H, PhCO), 7.7–7.4 (br m, 3 H, PhCO), 7.05 (t, J_{HH} = 7.0, 1 H, H^4), 6.8 (d, J_{HH} = 7.6 Hz, 1 H, H^3), 6.67 (t, J_{HH} = 7.4, 1 H, H^5) and 6.12 (d, J_{HH} = 7.6 Hz, 1 H, H^6).

Complex **1d**. Yield 236 mg (44%) [Found (Calc. for $C_{10}H_{11}ClN_2OPd$): C, 37.3 (37.98); H, 3.7 (3.51); N, 8.5 (8.86)%]. ^1H NMR: **1d**+C_5D_5N: δ 7.66 (s, 1 H, HC=N), 7.25 (d, J_{HH} = 7.2, 1 H, H^3), 7.00 (t, J_{HH} = 7.8, 1 H, H^4), 6.84 (t, J_{HH} = 7.8, 1 H, H^5), 6.74 (d, J_{HH} = 7.8 Hz, 1 H, H^6), 3.00 (s, 3 H, CH_3N) and 2.47 (s, 3 H, CH_3CO).

Complex **1e**. Yield 375 mg (67.3%) [Found (Calc. for $C_{11}H_{13}ClN_2OPd$): C, 38.8 (40.0); H, 4.0 (3.97); N, 8.3 (8.48)%]. ^1H NMR: **1e**+C_5D_5N, δ 9.10 (s, 1 H, NH), 7.04 (d, J_{HH} = 8.0, 1 H, H^4), 6.98 (s, 1 H, H^6), 6.73 (d, J_{HH} = 8.2 Hz, 1 H, H^3) 2.33 (s, 3 H, CH_3CO), 2.14 (s, 3 H, CH_3) and 1.97 (s, 3 H, CH_3CN).

Complex **1f**. Yield 292 mg (54.5%) [Found (Calc. for $C_{10}H_{11}ClN_2OPd$): C, 37.0 (37.98); H, 3.4 (3.50); N, 8.6 (8.86)%]. ^1H NMR: **1f**+C_5D_5N, δ 9.23 (s, 1 H, NH), 7.34 (d, J_{HH} = 7.8, 1 H, H^3), 7.19 (d, J_{HH} = 8.0, 1 H, H^6), 7.02 (t, J_{HH} = 7.8, 1 H, H^4), 6.75 (t, J_{HH} = 7.2 Hz, 1 H, H^5), 2.42 (s, 3 H, CH_3CO) and 2.07 (s, 3 H, CH_3CN).

Complex **1g**. Yield 295 mg (50.3%) [Found (Calc. for $C_{11}H_{13}ClN_2O_2Pd$): C, 37.7 (38.15); H, 4.0 (3.78); N, 7.9 (8.09)%]. ^1H NMR: **1g**+C_5D_5N, δ 9.11 (s, 1 H, NH), 7.14 (d, J_{HH} = 7.7, 1 H, H^3), 6.94 (s, 1 H, H^6), 6.60 (d, J_{HH} = 7.7 Hz, 1 H, H^4), 3.73 (s, 3 H, CH_3O), 2.42 (s, 3 H, CH_3CO) and 2.06 (s, 3 H, CH_3CN).

Complex **1h**. Yield 324 mg (50.6%) [Found (Calc. for $C_{15}H_{13}ClN_2OPd$): C, 46.8 (47.52); H, 3.2 (3.45); N, 7.1 (7.39)%].

Compounds 2. A stirred suspension of complex **1** (0.3 mmol) was treated with PPh_3 (0.6 mmol, 0.157 g) in acetone (30 cm^3) for 30 min at room temperature and then filtered. The filtrate was concentrated *in vacuo* and the deep orange solid obtained after addition of diethyl ether was recrystallized from chloroform–ether to obtain **2**.

Complex **2a**. Yield 262 mg (75%) [Found (Calc. for $C_{27}H_{23}ClN_3O_3PPd$): C, 53.2 (53.20); H, 3.6 (3.80); N, 6.7 (6.89)%]. Mass spectrum: m/z = 574 (M − Cl). ^1H NMR: δ 14.07 (d, J_{HP} = 3.5, 1 H, NH), 8.27 (d, J_{HP} = 4.0, 1 H, HC=N), 7.90–7.34 (br m, 16 H, H^3, PPh_3), 7.22 (dd, J_{HH} = 7.2, 2.0, 1 H, H^4), 6.76 (d, J_{HH} = 8.8 Hz, 1 H, H^6) and 2.42 (s, 3 H, CH_3CO). ^{31}P NMR: δ 42.17.

Complex **2b**. Yield 192 mg (57%) [Found (Calc. for $C_{27}H_{23}BrClN_2OPPd$): C, 50.3 (50.47); H, 3.5 (3.61); N, 4.3 (4.36)%]. ^1H NMR: δ 14.17 (d, J_{HP} = 3.0, 1 H, NH), 8.15 (d, J_{HP} = 3.5 Hz, 1 H, HC=N), 7.80–7.35 (br m, 15 H, PPh_3), 6.98 (dd, J_{HH} = 8.0, 2.0, 1 H, H^4), 6.60 (d, J_{HH} = 8.2 Hz, 1 H, H^3), 6.28 (dd, J_{HH} = 7.2, J_{HP} = 3.5 Hz, 1 H, H^6) and 2.26 (s, 3 H, CH_3CO). ^{31}P NMR: δ 42.45.

Complex **2c**. A stirred suspension of complex **1c** (0.3 mmol) was treated with PPh_3 (0.3 mmol, 0.065 g) in acetone (30 cm^3) for 30 min at room temperature and then filtered. The filtrate was concentrated *in vacuo* and the deep orange solid obtained after addition of ether was recrystallized from chloroform–ether to obtain **2c**. (103 mg, 30%) [Found (Calc. for $C_{32}H_{26}ClN_2OPPd$): C, 61.1 (61.33); H, 4.1 (4.18); N, 4.5 (4.47)%]. ^1H NMR: δ 9.09 (d, J_{HP} = 3.6, 1 H, HC=N), 8.07 (dd, J_{HH} = 7.7, 1.0 Hz; 2 H, PhCO), 7.9–7.3 (br m, 18 H, PPh_3, PhCO), 6.9–6.8 (m, 2 H, H^3, H^4) and 6.4–6.3 (m, 2 H, H^5, H^6). ^{31}P NMR: δ 43.94.

Compounds 3. A stirred suspension of complex **1** (0.3 mmol) was treated with PPh_3 (1.2 mmol, 0.314 g) in acetone (30 cm^3) for 30 min at room temperature and then filtered. The filtrate

was concentrated *in vacuo* and the deep yellow solid obtained after addition of ether was recrystallized from chloroform–ether to obtain **3**.

Complex **3d**. Yield 298 mg (56%) [Found (Calc. for $C_{46}H_{41}ClN_2OP_2Pd$): C, 65.1 (65.70); H, 4.9 (4.92); N, 3.2 (3.33)%]. ^{1}H NMR: δ 7.75–7.24 (br m, 30 H, PPh_3), 6.82 (dd, J_{HH} = 7.6, 1.0 Hz, 1 H, H^3), 6.63–6.57 (m, 3 H, HC=N, H^6, H^4), 6.13 (td, J_{HH} = 7.8, 1.8, 1 H, H^5), 3.27 (s, 3 H, CH_3N) and 2.07 (s, 3 H, CH_3CO). ^{31}P NMR: δ 20.85.

Complex **3e**. Yield 372 mg (72%) [Found (Calc. for $C_{47}H_{43}ClN_2OP_2Pd$): C, 66.0 (66.10); H, 5.0 (4.96); N, 3.3 (3.28)%]. ^{1}H NMR: δ 8.39 (s, 1 H, NH), 7.75–7.20 (br m, 30 H, PPh_3), 6.42–6.27 (m, 3 H, H^3, H^4, H^6), 2.21 (s, 3 H, CH_3CO), 1.81 (s, 3 H, CH_3CN) and 1.66 (s, 3 H, CH_3). ^{31}P NMR: δ 24.58.

Complex **3f**. Yield 452 mg (85%) [Found (Calc. for $C_{46}H_{41}ClN_2OP_2Pd$): C, 64.3 (65.70); H, 4.8 (4.91); N, 3.5 (3.33)%]. ^{1}H NMR: δ 8.41 (s, 1 H, NH), 7.72–7.20 (br m, 30 H, PPh_3), 6.74 (d, J_{HH} = 7.4, 1 H, H^3), 6.55 (t, J_{HH} = 7.0, 1 H, H^4), 6.48 (t, J_{HH} = 7.0, 1 H, H^5), 6.09 (td, J_{HH} = 8.5, J_{HP} = 1.0 Hz, 1 H, H^6), 2.20 (s, 3 H, CH_3CO) and 1.85 (s, 3 H, CH_3CN). ^{31}P NMR: δ 24.54.

Complex **3g**. Yield 430 mg (85%) [Found (Calc. for $C_{47}H_{43}ClN_2O_2P_2Pd$): C, 63.9 (64.81); H, 4.9 (4.98); N, 3.1 (3.21)%]. ^{1}H NMR: δ 8.31 (s, 1 H, NH), 7.75–7.21 (br m, 30 H, PPh_3), 6.44 (d, J_{HH} = 8.6 Hz, 1 H, H^3), 6.18–6.10 (m, 2 H, H^4, H^6), 3.23 (s, 3 H, OCH_3), 2.19 (s, 3 H, CH_3CO) and 1.81 (s, 3 H, CH_3CN). ^{31}P NMR: δ 24.52.

Complex **3h**. Yield 318 mg (67%) [Found (Calc. for $C_{51}H_{43}ClN_2OP_2Pd$): C, 66.9 (67.84); H, 4.9 (4.80); N, 3.2 (3.10)%]. ^{1}H NMR: δ = 7.76 (d, J_{HH} = 7.5, 2 H, PhCO), 7.75–7.16 (br m, 33 H, PPh_3, PhCO), 6.81 (s, 1 H, HC=N), 6.66 (d, J_{HH} = 6.5, 1 H, H^3), 6.59–6.55 (m, 2 H, H^6, H^4), 6.03 (t, J_{HH} = 7.0 Hz, 1 H, H^5) and 3.58 (s, 3 H, CH_3N). ^{31}P NMR: δ 21.07.

Compounds 4. Sodium methoxide (0.34 mmol, 0.0184 g) was added to a solution of complex **2a**, **2c** or **3e** (0.34 mmol) in methanol (30 cm^3) and the mixture was stirred under nitrogen for 2 h at room temperature. The solvent was removed *in vacuo* and the residue washed with ether (2 × 10 cm^3) and then recrystallized from chloroform–methanol to obtain **4**, as a violet solid.

Complex **4a**. Yield 148 mg (79%) [Found (Calc. for $C_{27}H_{22}N_3O_3PPd$): C, 56.5 (56.51); H, 3.9 (3.86); N, 7.3 (7.32)%]. Mass spectrum: *m*/*z* = 573 (*M*). ^{1}H NMR: δ 7.64 (dd, J_{HH} = 7.5, 2.0, 1 H, H^4), 7.59–7.44 (br m, 15 H, PPh_3), 6.99 (d, J_{HH} = 7.5, 1 H, H^3), 6.72 (s, 1 H, HC=C), 6.57 (d, J_{HP} = 2.0 Hz, 1 H, H^6) and 2.04 (s, 3 H, CH_3CO). ^{31}P: δ NMR 32.09.

Complex **4c**. Yield 167 mg (88.7%) [Found (Calc. for $C_{32}H_{25}N_2OPPd$: C, 64.4 (65.04); H, 4.3 (4.26); N, 4.7 (4.74)%]. ^{1}H NMR: δ 7.71–7.35 (br m, 21 H, HC=C, PhCO, PPh_3), 7.14 (d, J_{HH} = 7.6, 1 H, H^3), 6.81 (t, J_{HH} = 7.8, 1 H, H^4), 6.21 (t, J_{HH} = 7.6, 1 H, H^5) and 5.93 (br m, 1 H, H^6). ^{31}P NMR: δ 33.48.

Complex **4e**. Yield 89 mg (68.7%) [Found (Calc. for $C_{29}H_{27}N_2OPPd$): C, 63.3 (62.54); H, 4.8 (4.88); N, 5.2 (5.03)%]. ^{1}H NMR: δ 7.65–7.40 (br m, 15 H, PPh_3), 7.00 (d, J_{HH} = 7.6, 1 H, H^3), 6.55 (d, J_{HH} = 7.6, 1 H, H^4), 5.50 (d, J_{HP} = 2.0, 1 H, H^6), 2.04 (s, 3 H, CH_3CO), 1.96 (s, 3 H, CH_3) and 1.61 (s, 3 H, CH_3C=C). ^{31}P NMR: δ 32.04.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (project PB 96-0164) and the Comissionat per a Universitats i Recerca (project 1995SGR 00044) for financial support.

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Received 6*th February* 1998; *Paper* 8/01076E